

Effect of epitaxial strain on the cation distribution in spinel ferrites CoFe_2O_4 and NiFe_2O_4 : a density functional theory study

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The effect of epitaxial strain on the cation distribution in spinel ferrites CoFe_2O_4 and NiFe_2O_4 is investigated by GGA+ U total energy calculations. We obtain a very strong (moderate) tendency for cation inversion in NiFe_2O_4 (CoFe_2O_4), in agreement with experimental bulk studies. This preference for the inverse spinel structure is reduced by tensile epitaxial strain, which can lead to strong sensitivity of the cation distribution on specific growth conditions in thin films. Furthermore, we obtain significant energy differences between different cation arrangements with the same degree of inversion, providing further evidence for recently proposed short range B site order in NiFe_2O_4 .

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The spinel ferrites CoFe_2O_4 (CFO) and NiFe_2O_4 (NFO) are insulating ferrimagnets with high magnetic ordering temperatures and large saturation magnetizations.^{1,2} This combination of properties is very attractive for a number of applications, such as magneto-electric heterostructures and spin-filter devices.³⁻⁷ These applications require the growth of high quality thin films of CFO and NFO on suitable substrates. However, the electronic and magnetic properties of the corresponding films can depend strongly on substrate, film thickness, and specific preparation conditions, and eventually differ drastically from the corresponding bulk materials. For example, both increased and decreased saturation magnetizations have been reported for thin films of CFO and NFO grown on different substrates at different growth temperatures.⁸⁻¹⁰ It has been suggested that the large increase in magnetization observed in some NFO films is due to the presence of Ni^{2+} on the tetrahedrally coordinated cation sites of the spinel crystal structure.^{8,9}

The spinel crystal structure (space group $Fd\bar{3}m$) contains two inequivalent cation sites, the tetrahedrally-coordinated A sites (T_d) and the octahedrally coordinated B sites (O_h). In the *normal* spinel structure, A and B sites are both occupied by a unique cation species. In the *inverse* spinel structure, the more abundant cation species (Fe^{3+} in the present case) occupies the tetrahedral A sites and 50 % of the octahedral B sites, whereas the remaining 50 % of B sites are occupied by the other cation species (Co^{2+} or Ni^{2+} in the present case). In practice, site occupancies can vary between these two cases, depending on specific preparation conditions, and the inversion parameter λ measures the fraction of less abundant cations on the B site sublattice, i.e. $\lambda = 0$ for the normal spinel structure and $\lambda = 1$ for complete inversion. Since in the ferrimagnetic Néel state of CFO and NFO the magnetic moments of the A and B sublattices are oriented antiparallel to each other, small changes in λ can lead to significant changes in magnetization.

Here, we use first principles density functional theory to clarify whether epitaxial strain can influence the distribution of cations over the two different cation sites in CFO and NFO. Such epitaxial strain is generally incorporated in thin films due to the mismatch of lattice constants between the film material and the substrate, and often leads to drastic changes of properties compared to the corresponding bulk materials.²

In order to accommodate different arrangements of cations on the tetrahedral and octahedral sites in our calculations, corresponding to different degrees of inversion, we use a unit cell described by body centered tetragonal lattice vectors containing four formula units

(f.u.) of CFO/NFO. The unstrained cubic case corresponds to $c/a = \sqrt{2}$. We are considering configurations corresponding to $\lambda = \{0, 0.5, 0.75, 1\}$, and in each case (except for the unique case $\lambda = 0$) we compare at least two different inequivalent cation arrangements. Similar to our previous investigation we fix the internal coordinates of the cations to their ideal values within the cubic spinel structure and fully relax the remaining internal anion parameters.^{11,12} We then introduce epitaxial strain by constraining the “in-plane” lattice constant a , and relax the “out-of-plane” lattice constant c and all internal anion parameters. We apply strains ranging from -4% to $+4\%$ relative to the relaxed a lattice constant. All our calculations are performed using the projector-augmented wave method¹³ implemented in the Vienna *ab initio* simulation package (VASP).¹⁴ We employ the generalized gradient approximation (GGA) according to Perdew, Burke and Ernzerhof¹⁵ together with the Hubbard “+ U ” correction according to Dudarev *et al.*,¹⁶ and $U_{\text{eff}} = 3 \text{ eV}$ applied to the d states on all transition metal cations.

The calculated energy differences with respect to the normal spinel structure for the unstrained case are shown in Figs. 1(a) and 1(c) for CFO and NFO, respectively. Different cation arrangements are denoted by their corresponding space group symmetry. For $\lambda = 0.75$ the resulting symmetries are very low and thus Pm/Pm^* mark two inequivalent configurations with the same space group. It can be seen that for both CFO and NFO the total energy decreases with increasing inversion, so that the fully inverse spinel structure ($\lambda = 1$) is energetically most favorable. The calculated energy difference between the normal spinel structure and the most favorable inverse configuration is 0.37 eV (1.78 eV) per two f.u. for CFO (NFO), in good agreement with the value of 0.339 eV reported for CFO by Hou *et al.*¹⁷ The much larger preference for the inverse spinel structure of NFO compared to CFO is consistent with the experimental observation that NFO samples usually exhibit complete inversion, whereas the exact degree of inversion in CFO depends on the heat treatment during sample preparation and can vary between 0.76-0.93.^{1,18} The same energetic preference also follows from a simple ligand-field analysis of the Ni^{2+} and Co^{2+} cations within octahedral and tetrahedral coordination.^{19,20} However, it can be seen from our first principles results that there are also significant energy differences between different cation arrangements corresponding to the same value of λ . This indicates the importance of other factors such as higher order ligand-field effects and local structural relaxations. We note that configurations in which the Co (Ni) cations are clustered together, i.e. configuration Pm^* for $\lambda = 0.75$ and

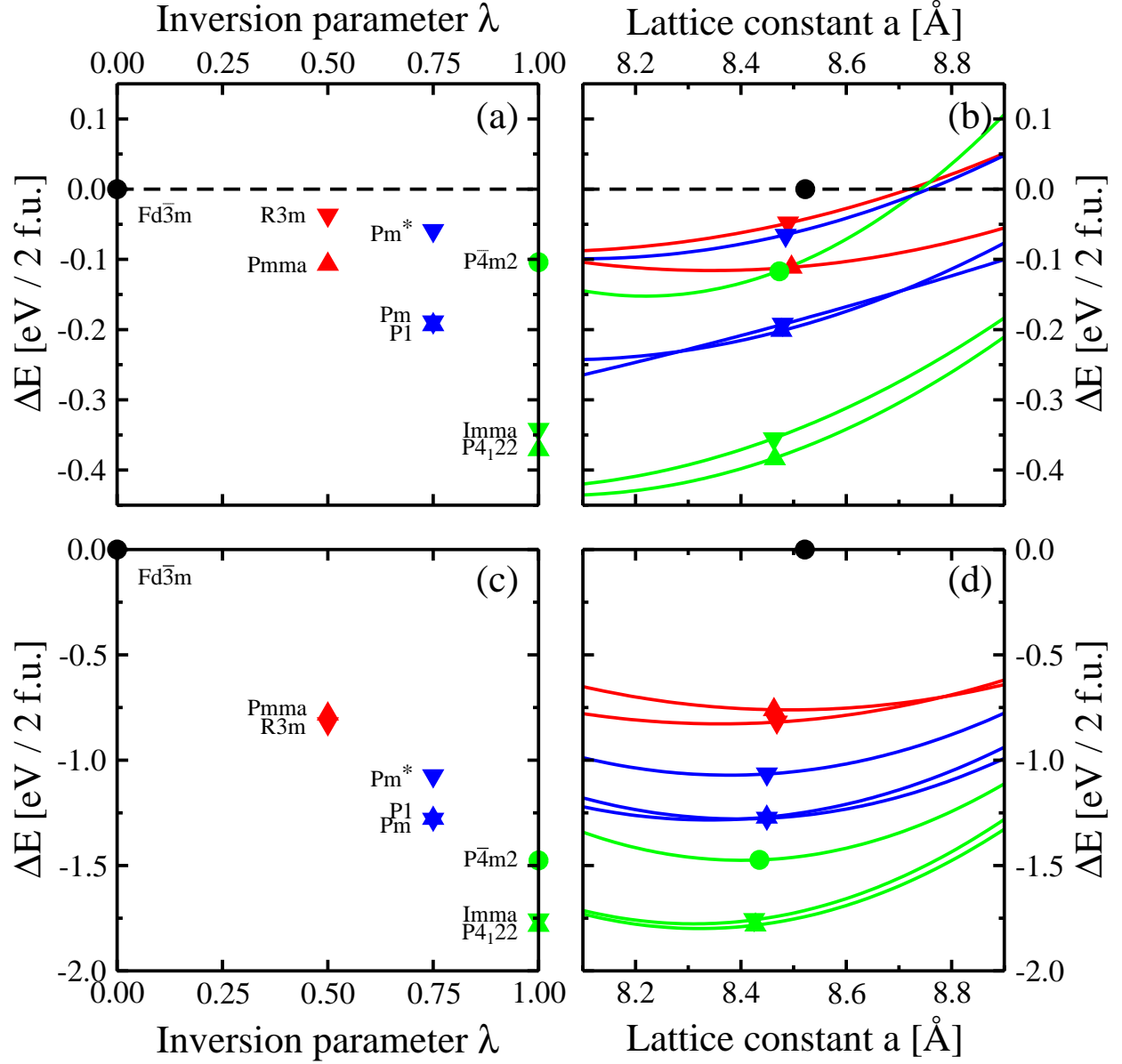


FIG. 1. (Color online) Calculated energy differences ΔE relative to the normal spinel structure for different cation arrangements corresponding to different inversion parameters λ for CFO (a) and NFO (c). Variation of ΔE with in-plane lattice constant a for CFO (b) and NFO (d) in the various configurations. The symbols in the right panels label different configurations and mark the corresponding equilibrium lattice constant.

$\text{P}\bar{4}\text{m}2$ for $\lambda = 1$, are energetically less favorable than configurations where Co (Ni) cations are distributed more uniformly, in agreement with similar findings of Hou *et al.*¹⁷

Next we turn to the question of whether the cation distribution and degree of inversion

can be influenced by epitaxial strain. Figs. 1(b) and 1(d) show the energy differences of the strained structures relative to the energy of the strained normal spinel at the same in-plane lattice constant for CFO and NFO, respectively. It can be seen that the equilibrium lattice constants decrease slightly with increasing λ . In addition, while full inversion is most favorable for all in-plane lattice parameters, the energy differences between different configurations decrease for larger in-plane lattice constants. For the case of NFO the energy difference between normal and inverse configuration reaches a maximum for $a \approx 8.3 \text{ \AA}$ and then decreases again for smaller in-plane lattice constants. From these results one can expect that CFO and NFO thin films under tensile strain are more likely to exhibit reduced inversion compared to unstrained or compressively strained films (assuming that they are otherwise grown under similar conditions). However, it is unclear whether the calculated moderate changes in the relative energies will indeed have a noticeable effect, or whether the actual cation distribution in thin films is rather dominated by kinetic effects related to specific growth conditions.

We also note that recent Raman investigations of both NFO single crystals²¹ and NFO thin films²² have provided evidence for short range cation order on the B sites compatible with $P4_122$ symmetry (or equivalently $P4_322$). Indeed, we find this to be the lowest energy configuration for both CFO and NFO over the whole investigated strain region. The energy difference compared to the *Imma* configuration in the unstrained structures is 28 meV (26 meV) per two f.u. for CFO (NFO). The structural preference for $P4_122$ symmetry is slightly increased by tensile epitaxial strain in the case of NFO, whereas for CFO the corresponding energy difference is rather independent of strain.

We now investigate the influence of cation inversion on the electronic structure of CFO and NFO. We obtain insulating ground states for all considered configurations. However, there is a strong tendency of the GGA+ U calculations to converge to higher energy states with low-spin and/or conducting character, depending on the initial positions for the structural relaxation.²³ Fig. 2 shows the densities of states (DOS) for CFO and NFO corresponding to the lowest-energy configurations for each λ . No significant differences in electronic structure for different cation arrangements with the same λ have been observed. The gradual exchange of Co^{2+} (Ni^{2+}) cations from the A site with Fe^{3+} cations from the B site with increasing inversion, is reflected in the DOS by a decreasing intensity of Co (Ni) T_d and Fe O_h peaks, and a corresponding increasing intensity of Co (Ni) O_h and Fe T_d peaks. In

addition, the band gap of CFO (NFO) increases from 0.22 eV (0.35 eV) for $\lambda = 0$ to 1.24 eV (1.26 eV) for $\lambda = 1$.

The spin-splitting of the conduction band minimum (CBM), which is important for the spin filter efficiency of magnetic tunnel junctions containing CFO or NFO as active barrier materials, is 0.47 eV for both CFO and NFO in the fully inverse structure. This is significantly smaller than the value of 1.28 eV (1.21 eV) for CFO (NFO), reported by Szotek *et al.*,²⁴ and is in good agreement to recent experimental estimates in the tens of meV for CFO-containing junctions.⁷ The CBM spin-splitting in CFO increases to 0.66 eV for $\lambda = 0.75$, which is closer to the value of $\lambda \sim 0.8$ observed recently in thin CFO films.¹⁸

In summary we have analyzed the effect of epitaxial strain on the cation distribution in the spinel ferrites CFO and NFO using first principles total energy calculations. Using the GGA+ U approach we obtain insulating electronic ground states for all degrees of inversion and cation arrangements, and for all considered values of epitaxial strain. We find a strong preference for the fully inverse structure in NFO, and a somewhat weaker tendency towards cation inversion in CFO, consistent with experimental observations. Tensile epitaxial strain reduces this preference somewhat, which can lead to a stronger sensitivity of the cation distribution on growth conditions. Furthermore, for both NFO and CFO we find the (fully inverse) B site ordered arrangement with $P4_122$ symmetry to be energetically most favorable, consistent with recent experimental results for NFO.^{21,22} Our results provide a reference for the interpretation of experimental data on CFO and NFO thin films, and thus contribute to a better understanding of these materials as part of magnetic tunnelling junctions and spin-filter devices.

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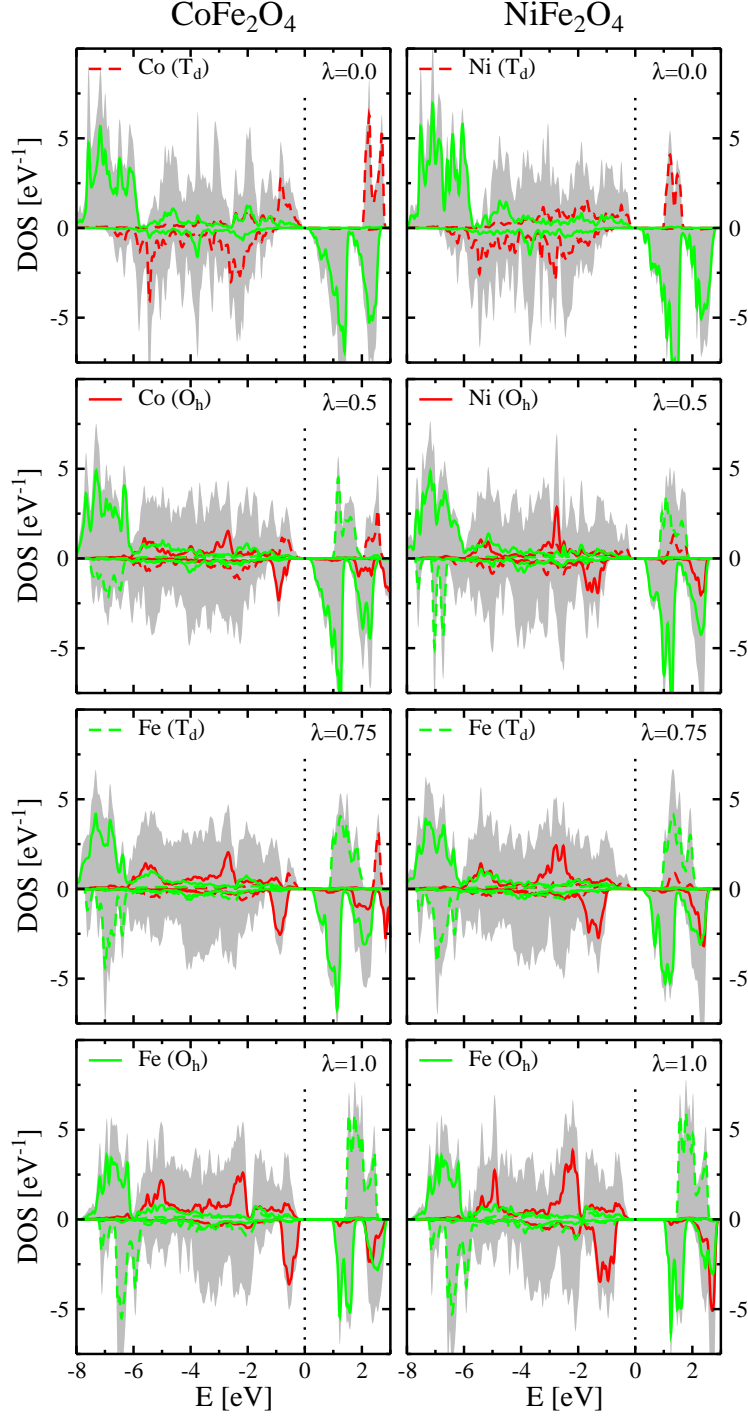


FIG. 2. (Color online) Total and projected DOS per formula unit for CFO (left panels) and NFO (right panels) for the lowest energy configurations corresponding to different λ . The d states of (Co, Ni) (O_h) and (T_d) are shown as solid and dashed red (black) lines, whereas d states of Fe (O_h) and (T_d) are shown as solid and dashed green (dark gray) lines, respectively. The total DOS is shown as shaded gray area in all panels. Majority (minority-) spin projections correspond to positive (negative) values.